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Abstract

Nanocomposites are becoming more and more popular and mechanical models are needed to help with their design and optimization. One of the key issues to be addressed by such models is the surface-stresses arising at the inclusion-matrix boundary, due to its high curvature. In this paper, we show that, contrary to what has previously been suggested, polarization techniques can be employed in the context of composites with interface effects. This requires a specific mathematical treatment of the interface, which must be regarded as a thin elastic layer. We then apply the proposed general methods to the specific case of nanocomposites with *monodisperse* spherical inclusions, for which a lower bound on the bulk modulus is derived. When interface effects are disregarded, this bound coincides with the classical Hashin-Shtrikman bound. In the presence of interface effects, we show that the existing Mori-Tanaka estimate is in fact a *lower-bound* on the effective bulk modulus. Finally, lower bounds on the effective bulk modulus of nanocomposites with *polydisperse* spherical inclusions are proposed. Although this result can be considered as a by-product of the previous one, it is new, and has no published Mori-Tanaka counterpart.

Key words: Nanocomposite, Surface stress, Hashin-Shtrikman bound, Spherical inclusion, Polarization

Introduction

In solid mechanics, imperfect solid-solid interfaces are usually thought of as surfaces where continuity of the traction vector is enforced, while displacements are discontinuous. Such interfaces can for instance represent ideal cracks in a continuous medium.

Another type of imperfect interfaces can however be devised, in which the displacements are continuous, but the traction vector undergoes a discontinuity. Such interface effects can arise in composite media, when coated inclusions are embedded in a matrix. If the coating is thin enough, it can be reduced to a surface (in the mathematical sense), and equilibrium of the finite-thickness

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coating asymptotically results in a generalized Laplace equation linking the discontinuity of bulk stresses to the stresses within the thin coating, see equations (14) and (15) in [1].

More generally, thermodynamical approach shows [2] that interface effects occur for *every* (even uncoated) solid-solid interface. The surface energy of conventional composites is usually negligible, compared to their bulk strain energy, and continuity of the traction vector can therefore still be assumed. Since surface energy depends on the surface area, this is no longer true for nanocomposites, due to the high surface-to-volume ratio of the inclusions. For this class of materials, surface effects cannot be disregarded, and experimental data indeed show a strong dependence of the macroscopic moduli with the size of the embedded nanoparticles [3, 4]. The stress discontinuities across the interface are now linked to so-called *surface-stresses* through generalized Young-Laplace equations [5, 6].

For both composites with coated inclusions, and nanocomposites, the stress jump can be assumed to depend linearly on the deformation of the interface. The *stiffness* of the interface can then be defined as a fourth-rank, surface tensor. This tensor will always be positive definite in the case of coated interfaces (since it derives from the 3d, positive definite, stiffness tensor of the material constituting the coating), whereas this could fail to be true for nanocomposites [7].

The determination of the effective mechanical properties of composites subjected to interface effects is of course of paramount interest. Based on the solution of a generalized Eshelby problem, combined with the Mori-Tanaka [8] or Generalized Self-Consistent [9] homogenization schemes, micromechanical estimates of the bulk and shear moduli of these composites have been proposed by various authors [10–12]; disregarding interface effects, other estimates have also been proposed [4, 13].

Besides estimates, rigorous *bounds* on the effective moduli are useful quantities allowing to check the consistency of the previous approximations. To the authors' knowledge, the only attempt at establishing bounds on the effective elastic moduli of a nanocomposite is due to Le Quang and He [14]. Restricting themselves to interfaces with positive definite stiffness, they derived first-order upper and lower bounds for the effective elastic moduli of a distribution of spheres. These bounds coincide with the well-known Voigt and Reuss bounds when interface effects are omitted. They concluded that second-order bounds of the Hashin-Shtrikman type [15] would be highly desirable, though difficult to arrive at, due to the peculiar (bidimensional) nature of the interface's stiffness tensor.

In this paper, we show how these difficulties can be overcome, and propose a general framework for the derivation of second-order bounds on the elastic moduli of composites with interface effects. In order to do so, we assume that the stiffness tensor of the interface is positive definite. This assumption is essential for the result to be valid. This general framework is then applied to a distribution of monosized spheres, for which we show that the Hashin-Shtrikman bound on the bulk modulus coincides with the Mori-Tanaka estimate derived by Duan et al. [11]. This remarkable result generalizes those available for a composite without interface effects.

Using the same ingredients, we finally explore the more general case of a polydisperse distribution of spherical nano-inclusions. We show that with little effort, the results obtained for monodisperse distributions can be extended to any particle-size distribution; the derivation then leads to a new general bound on the effective bulk modulus.

1. Background

1.1. Interface effects on spherical particles

At an interface between two different phases, the traction vector $\boldsymbol{\sigma} \cdot \mathbf{n}$ ($\boldsymbol{\sigma}$ is the stress tensor, $\mathbf{n}$ the normal to the interface) can undergo a discontinuity. In the case of a fluid-fluid interface for example, the Young-Laplace equation relates the pressure jump $[\![p]\!]$ across the interface to the surface tension γ and the local curvature $\mathbf{b}$

$$[\![p]\!] = \gamma \operatorname{tr} \mathbf{b}. \tag{1}$$

In the case of a solid-solid interface, not only the pressure, but also the shear stresses are discontinuous. Equilibrium of the interface then yields the following equation, which can be seen as a generalized Young-Laplace equation [5, 11]

$$[\![\boldsymbol{\sigma}]\!] \cdot \mathbf{n} + (\boldsymbol{\sigma}^s : \mathbf{b})\,\mathbf{n} + \nabla^s \cdot \boldsymbol{\sigma}^s = 0, \tag{2}$$

where ∇^s denotes the gradient operator along the interface, and $\boldsymbol{\sigma}^s$ the so-called *surface stress* tensor. This tensor accounts for the concentration of elastic energy in the vicinity of the interface [2]. Although this vicinity is of small, but finite, extension across the interface, it is convenient to reduce it to a mathematical surface. All related physical (bulk) quantities then become singular; in particular, this is true of the Cauchy stress tensor. Indeed, in terms of dimensional analysis, equation (2) shows that $\boldsymbol{\sigma}^s$ has dimension of volume stress $\times$ length. Going back to the physical origin of the surface stress tensor, and introducing the volume (Cauchy) stress $\boldsymbol{\sigma}^s_{3\mathrm{d}}$ within the interface $z^- \leq z \leq z^+$ of finite thickness $z^+ - z^-$, we have

$$\boldsymbol{\sigma}^s = \int_{z^-}^{z^+} \boldsymbol{\sigma}^s_{3\mathrm{d}}(z)\,\mathrm{d}z,$$

where z is the local coordinate perpendicular to the interface. When reducing the interface to a mathematical surface, the internal forces (stress resultants), which are the physically relevant quantity, must be conserved. The Cauchy stress within the interface must therefore be understood in the sense of generalized functions $\boldsymbol{\sigma}^s_{3\mathrm{d}}(z) = [\boldsymbol{\sigma}^s / (z^+ - z^-)]\,\delta(z)$. In turn, the use of such generalized functions can be sometimes misleading; this is certainly the case in the present study. When convenient, the (singular) surface stress will therefore be replaced by a fictitious volume stress *uniformly* distributed over a finite thickness h, which then tends to zero. This is the essence of the thin elastic layer analogy introduced in 1.3.

To sum up, we are faced with three different mathematical representations of the *same* physical problem

- real distribution of volume stresses $\boldsymbol{\sigma}^s_{3\mathrm{d}}(z)$ across the real interface $z^- \leq z \leq z^+$,
- singular surface stresses $\boldsymbol{\sigma}^s$ concentrated at the zero-thickness interface,
- fictitious volume stresses $\boldsymbol{\sigma}^s/h$ uniformly distributed over a fictitious interface of finite thickness h.

These representations are equivalent as long as the real thickness $z^+ - z^-$, as well as the fictitious thickness h are both small.

For spherical interfaces of radius a, to which this paper is devoted, the previous equation reads, in spherical coordinates (θ: inclination, φ: azimuth)

$$\sigma^s_{\theta\theta} + \sigma^s_{\varphi\varphi} - a\,[\![\sigma_{rr}]\!] = 0, \tag{3}$$

$$\partial_\theta \sigma^s_{\theta\theta} + \frac{1}{\sin\theta}\partial_\varphi \sigma^s_{\theta\varphi} + \left(\sigma^s_{\theta\theta} - \sigma^s_{\varphi\varphi}\right)\cot\theta + a\,[\![\sigma_{r\theta}]\!] = 0, \tag{4}$$

$$\partial_\theta \sigma^s_{\theta\varphi} + \frac{1}{\sin\theta}\partial_\varphi \sigma^s_{\varphi\varphi} + 2\,\sigma^s_{\theta\varphi}\cot\theta + a\,[\![\sigma_{r\varphi}]\!] = 0, \tag{5}$$

with $[\![\sigma_{ij}]\!] = \sigma_{ij}(r = a+, \theta, \varphi) - \sigma_{ij}(r = a-, \theta, \varphi)$.

As already indicated, a linearly elastic behavior of the interface is assumed. Under this assumption, the surface stresses are linearly related to the tangential components of the local strain tensor. For isotropic (in the 2d sense) elasticity, the general surface stress-bulk strain relationship can be found in Duan et al. [11], Le Quang and He [14], and specializes for spherical interfaces

$$\sigma^s_{\theta\theta} = \lambda^s\left(\varepsilon_{\theta\theta} + \varepsilon_{\varphi\varphi}\right) + 2\mu^s\varepsilon_{\theta\theta}, \tag{6}$$

$$\sigma^s_{\varphi\varphi} = \lambda^s\left(\varepsilon_{\theta\theta} + \varepsilon_{\varphi\varphi}\right) + 2\mu^s\varepsilon_{\varphi\varphi}, \tag{7}$$

$$\sigma^s_{\theta\varphi} = 2\,\mu^s\varepsilon_{\theta\varphi}, \tag{8}$$

where ε_{ij} denote the components (in spherical coordinates) of the local (bulk) strain tensor, and λ^s, μ^s the elasticity coefficients of the interface; we further introduce $\kappa^s = \lambda^s + \mu^s$. It should be noted that this last notation is fully consistent with Le Quang and He [14] ($\kappa^s = \kappa_{si}$; $\mu^s = \mu_{si}$), while it differs slightly from Duan et al. [11], who adopted $\kappa^s = 2(\lambda^s + \mu^s)$.

This constitutive law can be rewritten in intrinsic form

$$\boldsymbol{\sigma}^s = \mathbf{c}^s : \boldsymbol{\varepsilon}, \tag{9}$$

where $\mathbf{c}^s$ denotes the fourth-rank (2d) elasticity tensor of the interface. It relates a *volume* quantity ($\boldsymbol{\varepsilon}$, continuous across the interface) to a *surface* quantity ($\boldsymbol{\sigma}^s$). The elasticity tensor $\mathbf{c}^s$ has therefore the exact same singular nature as the surface tensor $\boldsymbol{\sigma}^s$. However, unlike the surface stress $\boldsymbol{\sigma}^s$, the surface stiffness $\mathbf{c}^s$ is simply a mathematical entity relating two measured quantities. As such, it has no physical volume counterpart; in particular, it is generally *not* the integral of a real stiffness tensor (although we will introduce a *fictitious* 3d stiffness tensor in 1.3). This is the reason why this tensor may not necessarily be positive definite, as already mentioned. Positive definiteness is essential in the framework of polarization methods, and we will therefore assume in this study that $\mathbf{c}^s$ *is* positive definite. More precisely, we will require the fictitious 3d stiffness tensor $\tilde{\mathbf{c}}^s$ to be positive definite, which, on closer inspection of (21) and (22), leads to

$$0 < \kappa^s < 3\mu^s. \tag{10}$$

1.2. Polarization methods in the absence of interface effects

In this section, we briefly introduce the variational methods developped by Willis [16] and Ponte-Castañeda and Willis [17]. In their original form, these methods cannot handle interface effects. How to include such effects in the framework presented here is the purpose of the next section.

Polarization methods require the introduction of a *reference* medium, which is assumed to be linearly elastic, homogeneous and isotropic, with stiffness $\mathbf{c}^0$. If this medium is *softer* than any of the - so far, 3d - phases included in the composite, the following inequality holds for any choice of the macroscopic strain $\mathbf{E}$ and the so-called *polarization* $\boldsymbol{\tau}(\mathbf{x})$ stress field [17]

$$\frac{1}{2}\,\mathbf{E} : \mathbf{C} : \mathbf{E} \geq \frac{1}{2}\,\mathbf{E} : \mathbf{c}^0 : \mathbf{E} + \overline{\boldsymbol{\tau}} : \mathbf{E} - \frac{1}{2}\,\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^0)^{-1} : \boldsymbol{\tau}} - \frac{1}{2}\,\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)}, \tag{11}$$

in which '$\circledast$' stands for the product of a two-point, fourth-rank operator with a one-point, second-rank tensor

$$\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}(\mathbf{x}) = \int_{\mathbf{y}\in\Omega} \boldsymbol{\Gamma}^0(\mathbf{x}, \mathbf{y}) : \boldsymbol{\tau}(\mathbf{y})\,\mathrm{d}^3 y, \tag{12}$$

while overlines denote volume averages

$$\overline{\mathcal{B}} = \frac{1}{V} \int_{\mathbf{x}\in\Omega} \mathcal{B}(\mathbf{x})\,\mathrm{d}^3 x, \tag{13}$$

$V = |\Omega|$ being the size of the representative volume element Ω. It should be noted at this point that inequality (11) holds for *any* choice of the polarization stress field $\boldsymbol{\tau}(\mathbf{x})$. Unlike other variational principles, no constraint is imposed on $\boldsymbol{\tau}$.

The Green operator for strains, $\boldsymbol{\Gamma}^0$, which appears in (11) is defined as follows [18]: for any choice of the polarization field $\boldsymbol{\tau}(\mathbf{x})$, $\boldsymbol{\varepsilon}(\mathbf{x}) = -\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}(\mathbf{x})$ is the strain field in a prestressed, homogeneous elastic medium with fixed boundary conditions

$$\operatorname{div}\left[\mathbf{c}^0 : \boldsymbol{\varepsilon}(\mathbf{x}) + \boldsymbol{\tau}(\mathbf{x})\right] = 0 \qquad (\mathbf{x} \in \Omega), \tag{14}$$

$$\varepsilon_{ij}(\mathbf{x}) = \frac{1}{2}\left[\partial_i u_j(\mathbf{x}) + \partial_j u_i(\mathbf{x})\right] \qquad (\mathbf{x} \in \Omega), \tag{15}$$

$$\mathbf{u}(\mathbf{x}) = 0 \qquad (\mathbf{x} \in \partial\Omega). \tag{16}$$

As pointed out by Willis [16], the finite-body Green operator $\boldsymbol{\Gamma}^0$ may be replaced by the infinite-body Green operator $\boldsymbol{\Gamma}^0_\infty$

$$\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}(\mathbf{x}) \simeq \int_{\mathbf{y}\in\Omega} \boldsymbol{\Gamma}^0_\infty(\mathbf{x} - \mathbf{y}) : [\boldsymbol{\tau}(\mathbf{y}) - \overline{\boldsymbol{\tau}}]\,\mathrm{d}^3 y \tag{17}$$

Assuming the representative volume element Ω to be of ellipsoidal shape, we then make use of Eshelby's theorem [19] which leads to

$$\int_{\mathbf{y}\in\Omega} \boldsymbol{\Gamma}^0_\infty(\mathbf{x} - \mathbf{y}) : \overline{\boldsymbol{\tau}}\mathrm{d}^3 y = \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}}, \tag{18}$$

where $\mathbf{P}^\Omega$ denotes the Hill tensor of the ellipsoid Ω. We finally find

$$\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)} = \frac{1}{V} \int_{\mathbf{x},\mathbf{y}\in\Omega} \boldsymbol{\tau}(\mathbf{x}) : \boldsymbol{\Gamma}^0_\infty(\mathbf{x} - \mathbf{y}) : \boldsymbol{\tau}(\mathbf{y})\,\mathrm{d}^3 x\,\mathrm{d}^3 y - \overline{\boldsymbol{\tau}} : \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}}. \tag{19}$$

To conclude this section, we note that if the reference medium is *stiffer* than all phases in the composite, then the sign of inequality (11) must be changed, leading to an upper bound on the effective elastic energy of the composite. As will be illustrated below, an appropriate choice of the polarization field $\boldsymbol{\tau}(\mathbf{x})$ (with an isotropic macroscopic strain $\mathbf{E}$) can lead to upper- and lower-bounds on the macroscopic bulk modulus of a composite.

1.3. The interface as a thin elastic layer

The stiffness tensor $\mathbf{c}^s$ defined by (9) is a *surface* tensor. As such, it cannot be directly compared with the stiffness of the matrix and the inclusions (which are 3d tensors). In order to establish Hashin-Shtrikman type bounds, however, we need to be able to compare the stiffnesses of all phases with the reference material (see third term on the right-hand side of (11)). Without further transformation, it is physically meaningless to compare the stiffness of the interface with the stiffness of the reference material. However, noting that equations (2) and (9) are in fact the basic equations of an elastic layer of small, but finite thickness, we show in this section that it is possible to introduce a 3d stiffness tensor $\tilde{\mathbf{c}}^s$ accounting for the interface. The quantity $\tilde{\mathbf{c}}^s - \mathbf{c}^0$ then becomes mathematically meaningful.

Following the approach of Hashin [1], the elastic interface in the two-phase model (matrix + inclusions) is represented by an elastic *layer* of small, but finite, thickness $h \ll a$, made of an isotropic, linearly elastic material with Young modulus E, and Poisson ratio ν. In Appendix A, we show that if

$$\kappa^s = \frac{E h}{2(1-\nu)}, \qquad \mu^s = \frac{E h}{2(1+\nu)}, \tag{20}$$

then the two- and three-phase models are asymptotically equivalent when $h \to 0+$.

The 3d bulk and shear moduli $\tilde{\kappa}^s$ and $\tilde{\mu}^s$ of the equivalent elastic layer are then deduced from their 2d counterparts by

$$\tilde{\kappa}^s = \frac{E}{3(1-2\nu)} = \frac{4\kappa^s \mu^s}{3h(3\mu^s - \kappa^s)}, \tag{21}$$

$$\tilde{\mu}^s = \frac{E}{2(1+\nu)} = \frac{\mu^s}{h}, \tag{22}$$

and the corresponding 3d stiffness tensor reads

$$\tilde{\mathbf{c}}^s = 3\tilde{\kappa}^s \mathbf{J} + 2\tilde{\mu}^s \mathbf{K}, \tag{23}$$

where $\mathbf{J}$ and $\mathbf{K}$ are the spherical and deviatoric fourth-order projectors.

When convenient, surface integrals involving the 2d stiffness tensor $\mathbf{c}^s$ will be replaced by analogous volume integrals involving the 3d stiffness tensor $\tilde{\mathbf{c}}^s$. As for polarizations, the 2d polarization tensor $\boldsymbol{\tau}^s$ should accordingly be replaced by the 3d polarization tensor $\boldsymbol{\tau}^s/h$. The limit when $h \to 0+$ must then be taken in the subsequent expressions.

2. Application to nanocomposites with mono-sized spherical inclusions

In their standard form, polarization methods cannot handle interface effects. In this section, we make use of the equivalence developed in section 1.3 to overcome this shortcoming. We consider here a distribution of spherical inclusions (superscript 'i') of radius a, embedded in a matrix (superscript 'm'). The stiffness tensor of the inclusions (resp. the matrix) is denoted $\mathbf{c}^i$ (resp. $\mathbf{c}^m$). Let us also assume that the interface stiffness is positive definite, i.e. that (10) is verified. The 3d stiffness tensor $\tilde{\mathbf{c}}^s$ of the equivalent layer defined by (21), (22) and (23) is therefore also positive definite, and the polarization methods introduced in section 1.2 apply, with the matrix as reference material ($\mathbf{c}^0 = \mathbf{c}^m$). It should be noted that usually in nanocomposites, the inclusions are stiffer than the matrix; besides, the thickness h of the equivalent layer being arbitrarily small, this fictitious layer is also stiffer than the matrix and the inclusions. It follows that

$$\mathbf{c}^m \leq \mathbf{c}^i \leq \tilde{\mathbf{c}}^s, \tag{24}$$

where $\mathbf{c} \leq \mathbf{c}'$ means that the difference $\mathbf{c}' - \mathbf{c}$ is a positive semidefinite quadratic form. In other words, the reference medium is *softer* than all phases in the composite, and the polarization methods exposed in section 1.2 will lead to a *lower* bound on the effective elastic energy of the nanocomposite.

2.1. General form for the polarization field

Let us first recall that classical Hashin-Shtrikman bounds are obtained with piecewise constant polarization fields. In our case, such a simple structure for $\boldsymbol{\tau}$ proves too restrictive, and we will need to allow for a dependence of the polarization field on the spherical angles. It should be noted that the reference medium coincides with the matrix, therefore $\mathbf{c}^m - \mathbf{c}^0$ is singular. Due to the third term of the right-hand side of equation (11), namely

$$\frac{1}{2}\,\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^0)^{-1} : \boldsymbol{\tau}}, \tag{25}$$

the polarization must vanish in the matrix [17].

Let N be the number of (spherical) nanoparticles contained in the representative volume element Ω. Particle α ($\alpha = 1, \ldots, N$) is centered at point $\mathbf{x}^\alpha$. In this paper, we consider polarization fields $\boldsymbol{\tau}$ of the form

$$\boldsymbol{\tau}(\mathbf{x}) = \sum_{\alpha=1}^{N} \boldsymbol{\tau}^p(\mathbf{x} - \mathbf{x}^\alpha), \tag{26}$$

where $\boldsymbol{\tau}^p$ denotes the polarization applied to each single particle (one particle being defined as the union of inclusion *and* interface), which is the sum of two terms

$$\boldsymbol{\tau}^p(\mathbf{x}) = \mathrm{H}\,(a - r)\,\boldsymbol{\tau}^i(\mathbf{x}) + \delta(r - a)\boldsymbol{\tau}^s(\mathbf{n}), \tag{27}$$

where $r = |\mathbf{x}|$ and $\mathbf{n} = \mathbf{x}/r$; H is the Heaviside function, and δ the Dirac generalized function. $\boldsymbol{\tau}^i$ is the polarization on the inclusion, while $\boldsymbol{\tau}^s$ is the polarization on the interface. It will be convenient to introduce the volume average of $\boldsymbol{\tau}^i$, as well as the angular average of $\boldsymbol{\tau}^s$

$$\overline{\boldsymbol{\tau}}^i = \frac{1}{v} \int_{|\mathbf{x}| \leq a} \boldsymbol{\tau}^i(\mathbf{x})\,\mathrm{d}^3 x, \tag{28}$$

$$\overline{\boldsymbol{\tau}}^s = \frac{1}{4\pi} \int_{|\mathbf{n}|=1} \boldsymbol{\tau}^s(\mathbf{n})\,\mathrm{d}^2 n, \tag{29}$$

where $v = 4/3\pi a^3$ denotes the volume of the nanoparticles. The volume average of the total polarization $\boldsymbol{\tau}$ then reads

$$\overline{\boldsymbol{\tau}} = f\,\overline{\boldsymbol{\tau}}^i + \frac{3f}{a}\,\overline{\boldsymbol{\tau}}^s, \tag{30}$$

where $f = Nv/V$ is the volume fraction of nanoparticles.

2.2. *Bound on the bulk modulus*

In order to obtain a bound on the bulk modulus of the composite, we choose

$$\mathbf{E} = \frac{1}{3}E\mathbf{i}, \qquad \boldsymbol{\tau}^i = \tau^i\mathbf{i}, \qquad \boldsymbol{\tau}^s(\mathbf{x}) = \tau^s\,(\mathbf{i} - \mathbf{n}\otimes\mathbf{n}), \tag{31}$$

where $\mathbf{i}$ denotes the second-rank identity tensor. The averages of $\boldsymbol{\tau}^i$ and $\boldsymbol{\tau}^s$ defined by (28) and (29) then read

$$\overline{\boldsymbol{\tau}}^i = \tau^i\,\mathbf{i}, \quad \overline{\boldsymbol{\tau}}^s = \frac{2}{3}\tau^s\,\mathbf{i}, \quad \overline{\boldsymbol{\tau}} = f\left(\tau^i + \frac{2\tau^s}{a}\right)\mathbf{i}. \tag{32}$$

Introducing (31) and (32) in the right-hand side of (11), whose four terms must be evaluated (see below), we obtain a bound on the bulk modulus of the composite.

We start with the two terms $\mathbf{E} : \mathbf{C} : \mathbf{E}$ and $\mathbf{E} : \mathbf{c}^m : \mathbf{E}$, whose evaluation is straightforward

$$\mathbf{E} : \mathbf{C} : \mathbf{E} = KE^2, \qquad \mathbf{E} : \mathbf{c}^m : \mathbf{E} = \kappa^m E^2, \tag{33}$$

where K (resp. κ^m) denotes the effective bulk modulus of the composite (resp. the matrix). Then, equation (32) immediately yields

$$\overline{\boldsymbol{\tau}} : \mathbf{E} = f\left(\tau^i + \frac{2\tau^s}{a}\right)E \tag{34}$$

As for the term $\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}}$, using (26), we first find

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = \frac{1}{V}\sum_{\alpha=1}^{N}\int_{|\mathbf{x}-\mathbf{x}^\alpha|\le a} \boldsymbol{\tau}^p(\mathbf{x}-\mathbf{x}^\alpha) : \left[\mathbf{c}(\mathbf{x}) - \mathbf{c}^m\right]^{-1} : \boldsymbol{\tau}^p(\mathbf{x}-\mathbf{x}^\alpha)\,\mathrm{d}^3x, \tag{35}$$

where it has been assumed that each nanoparticle is completely included in the representative volume element Ω. Since for $|\mathbf{x} - \mathbf{x}^\alpha| \le a$, $\mathbf{c}(\mathbf{x})$ depends only on $\mathbf{x} - \mathbf{x}^\alpha$, all N terms in the right hand side of (35) are in fact identical

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = \frac{N}{V}\int_{|\mathbf{x}|\le a} \boldsymbol{\tau}^p(\mathbf{x}) : \left[\mathbf{c}(\mathbf{x}) - \mathbf{c}^m\right]^{-1} : \boldsymbol{\tau}^p(\mathbf{x})\,\mathrm{d}^3x. \tag{36}$$

As already noted in section 1.3, we need to be able to compare the stiffness of the interface and the stiffness of the solid matrix. In order to do so, we treat the interface as an elastic layer of thickness h, and stiffness $\tilde{\mathbf{c}}^s$. $\boldsymbol{\tau}^s$ must then be replaced by $\boldsymbol{\tau}^s/h$

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = \frac{N}{V}\int_{|\mathbf{x}|\le a} \boldsymbol{\tau}^i : \left(\mathbf{c}^i - \mathbf{c}^m\right)^{-1} : \boldsymbol{\tau}^i\,\mathrm{d}^3x + \dots$$
$$\dots + \frac{N}{V}\int_{a\le|\mathbf{x}|\le a+h} \frac{\boldsymbol{\tau}^s}{h} : (\tilde{\mathbf{c}}^s - \mathbf{c}^m)^{-1} : \frac{\boldsymbol{\tau}^s}{h}\,\mathrm{d}^3x. \tag{37}$$

The first term reduces to $\left(\tau^i\right)^2 f/\left(\kappa^i - \kappa^m\right)$, while spherical coordinates $\mathbf{x} = r\,\mathbf{n}$ are used for the integration of the second term (integration with respect to r being trivial when $h \ll a$)

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = f\,\frac{\left(\tau^i\right)^2}{\kappa^i - \kappa^m} + \frac{N}{V}\frac{1}{h}\left(a^2 + \frac{h^2}{12}\right)\int_{|\mathbf{n}|=1} \boldsymbol{\tau}^s(\mathbf{n}) : (\tilde{\mathbf{c}}^s - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}^s(\mathbf{n})\,\mathrm{d}^2n. \tag{38}$$

Since the limit $h \to 0+$ is to be taken in expression (38), equations (21) and (22) show that $(\tilde{\mathbf{c}}^s - \mathbf{c}^m)^{-1}$ can be replaced with $(\tilde{\mathbf{c}}^s)^{-1}$, and simple algebra leads to

$$\boldsymbol{\tau}^s(\mathbf{n}) : (\tilde{\mathbf{c}}^s)^{-1} : \boldsymbol{\tau}^s(\mathbf{n}) = \frac{h}{\kappa^s}\,(\tau^s)^2\,, \tag{39}$$

and finally, with $h \to 0+$,

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = f\,\frac{\left(\tau^i\right)^2}{\kappa^i - \kappa^m} + \frac{3f}{a}\,\frac{(\tau^s)^2}{\kappa^s}. \tag{40}$$

Finally, the last term in (11), namely $\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)}$, is evaluated. Using equations (19) and (26), we get

$$\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)} = \frac{1}{V}\sum_{\alpha,\beta=1}^{N}\int_{\mathbf{x},\mathbf{y}} \boldsymbol{\tau}^p(\mathbf{x} - \mathbf{x}^\alpha) : \boldsymbol{\Gamma}^m_\infty(\mathbf{x} - \mathbf{y}) : \boldsymbol{\tau}^p(\mathbf{y} - \mathbf{x}^\beta)\,\mathrm{d}^3x\,\mathrm{d}^3y - \overline{\boldsymbol{\tau}} : \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}}. \tag{41}$$

Replacing $\mathbf{x}$ by $\mathbf{x} + \mathbf{x}^\beta$, and $\mathbf{y}$ by $\mathbf{y} + \mathbf{x}^\beta$,

$$\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)} = \frac{1}{V}\sum_{\alpha,\beta=1}^{N}\int_{\mathbf{x},\mathbf{y}} \boldsymbol{\tau}^p\left[\mathbf{x} - \left(\mathbf{x}^\alpha - \mathbf{x}^\beta\right)\right] : \boldsymbol{\Gamma}^m_\infty(\mathbf{x} - \mathbf{y}) : \boldsymbol{\tau}^p(\mathbf{y})\,\mathrm{d}^3x\,\mathrm{d}^3y - \overline{\boldsymbol{\tau}} : \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}}. \tag{42}$$

Equation (B.13) shows that in the previous sum, all terms with $\alpha \neq \beta$ vanish. Moreover, (B.8) gives the value of this term for $\alpha = \beta$. Then, assuming the representative volume element Ω to be spherical, $\mathbf{P}^\Omega$ is known [19]. We finally find

$$\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)} = 3f\,(1 - f)\,\frac{\left(\tau^i + 2\tau^s/a\right)^2}{3\kappa^m + 4\mu^m}. \tag{43}$$

We now seek the best choice of polarizations τ^i and τ^s leading to the optimal bound on K. Gathering equations (33), (34), (40) and (43), we find the following inequality, valid for any choice of E, τ^i and τ^s

$$\frac{1}{2}\,KE^2 \geq \frac{1}{2}\,\kappa^m E^2 + f\left(\tau^i + \frac{2\tau^s}{a}\right)E - \frac{f}{2}\,\frac{\left(\tau^i\right)^2}{\kappa^i - \kappa^m} - \frac{3f}{2a}\,\frac{(\tau^s)^2}{\kappa^s} - \frac{3}{2}\,f\,(1 - f)\,\frac{\left(\tau^i + 2\tau^s/a\right)^2}{3\kappa^m + 4\mu^m}. \tag{44}$$

When the macroscopic strain E is fixed, the quantity on the right hand side of (44) is a quadratic form of the two variables τ^i and τ^s. Direct optimization with respect to these two variables is possible, but it is preferable to introduce the following auxiliary variables

$$\tau = \tau^i + \frac{2\tau^s}{a}, \qquad \tau' = \tau^i - \frac{3}{2}\,\frac{\kappa^i - \kappa^m}{\kappa^s}\,\tau^s. \tag{45}$$

It follows that

$$\frac{\left(\tau^i\right)^2}{\kappa^i - \kappa^m} + \frac{3}{a}\,\frac{(\tau^s)^2}{\kappa^s} = \frac{1}{\kappa^p - \kappa^m}\left(\tau^2 + \frac{4\kappa^s/3a}{\kappa^i - \kappa^m}\,\tau'^2\right), \tag{46}$$

where

$$\kappa^p = \kappa^i + \frac{4\kappa^s}{3a} \tag{47}$$

and (44) can be rewritten as

$$\frac{1}{2}\,KE^2 \geq \frac{1}{2}\,\kappa^m E^2 + fE\tau - \frac{f}{2}\,\frac{1}{\kappa^p - \kappa^m}\left(\tau^2 + \frac{4\kappa^s/3a}{\kappa^i - \kappa^m}\,\tau'^2\right) - \frac{3}{2}\,f\,(1-f)\,\frac{\tau^2}{3\kappa^m + 4\mu^m}. \tag{48}$$

Clearly, this bound will be optimal for $\tau' = 0$, so that for any value of τ

$$\frac{1}{2}\,KE^2 \geq \frac{1}{2}\,\kappa^m E^2 + fE\tau - \frac{f}{2}\,\frac{\tau^2}{\kappa^p - \kappa^m} - \frac{3}{2}\,f\,(1-f)\,\frac{\tau^2}{3\kappa^m + 4\mu^m}. \tag{49}$$

Optimizing now with respect to τ leads to the following bound on the bulk modulus of the composite

$$K \geq \kappa^m + f\,\frac{3\kappa^m + 4\mu^m}{3f\kappa^m + 4\mu^m + 3\,(1-f)\,\kappa^p}\,\left(\kappa^p - \kappa^m\right). \tag{50}$$

It is interesting to note that this bound formally coincides with the classical Hashin-Shtrikman bound for composites with spherical inclusions (modified bulk modulus: κ^p) embedded in an homogeneous matrix (bulk modulus: κ^m, shear modulus: μ^m), *without surface effects*.

This bound can also be proved to coincide with the Mori-Tanaka estimate of Duan et al. [11]. In comparing with this paper, however, attention should be paid to the fact that our definition of κ^s differs from Duan's (see the end of section 1.1). This generalizes the well-known result that Hashin-Shtrikman bounds and Mori-Tanaka estimates coincide for spherical particulate composites in the absence of surface effects. Our calculation proves that it can be extended to composites with surface effects.

3. Extension to nanocomposites with polydisperse spherical inclusions

In this section, the above derivation is extended to polydisperse distributions of spherical inclusions. It is assumed that all particles (inclusions *and* their interface) share the same elastic moduli κ^i, μ^i, κ^s and μ^s; however, the radius a^α, $\alpha = 1, \ldots, N$, is specific to each inclusion. The particle-size distribution is characterized by the function f, such as $f\,(a)\,\mathrm{d}a$ is the volume fraction of all inclusions having a radius comprised between a and $a + \mathrm{d}a$; the total volume fraction of inclusions therefore reads

$$\int_0^{+\infty} f\,(a)\,\mathrm{d}a. \tag{51}$$

In order to exhibit a bound which explicitly accounts for the particle-size distribution, expressions (26), (27) and (31) are now replaced by the more general form

$$\boldsymbol{\tau}\,(\mathbf{x}) = \sum_{\alpha=1}^{N} \boldsymbol{\tau}^p\,(\mathbf{x} - \mathbf{x}^\alpha, a^\alpha)\,, \tag{52}$$

where

$$\boldsymbol{\tau}^p\,(\mathbf{x}, a) = \mathrm{H}\,(a - r)\,\tau^i\,(a)\,\mathbf{i} + \delta\,(r - a)\,\tau^s\,(a)\,(\mathbf{i} - \mathbf{n}\otimes\mathbf{n})\,, \tag{53}$$

and $r = |\mathbf{x}|$, $\mathbf{n} = \mathbf{x}/r$. In the above expression $\tau^i\,(a)$ and $\tau^s\,(a)$ are two arbitrary scalar functions of the radius a. Keeping the same value of the macroscopic strain tensor $\mathbf{E}$, see equation (31), the desired bound is derived from the introduction of (53) in the general inequality (11).

With the definition of $f(a)$ at hand, it can readily be seen that expressions (34) and (40) are still valid, provided that the volume fraction f is replaced by appropriate integrals of the function $f(a)$. It is found successively

$$\overline{\boldsymbol{\tau}} = \int_0^{+\infty} f(a)\left[\tau^i(a) + \frac{2}{a}\tau^s(a)\right]\mathrm{d}a\,\mathbf{i}, \tag{54}$$

$$\overline{\boldsymbol{\tau} : (\mathbf{c} - \mathbf{c}^m)^{-1} : \boldsymbol{\tau}} = \int_0^{+\infty} f(a)\left[\frac{\tau^i(a)^2}{\kappa^i - \kappa^m} + \frac{3}{a}\frac{\tau^s(a)^2}{\kappa^s}\right]\mathrm{d}a, \tag{55}$$

$$\left(\kappa^m + \frac{4}{3}\mu^m\right)\overline{\boldsymbol{\tau}} : \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}} = \left\{\int_0^{+\infty} f(a)\left[\tau^i(a) + \frac{2}{a}\tau^s(a)\right]\mathrm{d}a\right\}^2, \tag{56}$$

$$\left(\kappa^m + \frac{4}{3}\mu^m\right)\left[\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0 \circledast \boldsymbol{\tau}\right)} + \overline{\boldsymbol{\tau}} : \mathbf{P}^\Omega : \overline{\boldsymbol{\tau}}\right] = \int_0^{+\infty} f(a)\left[\tau^i(a) + \frac{2}{a}\tau^s(a)\right]^2\mathrm{d}a. \tag{57}$$

It should be noted that the proof of (57) relies on the use of (B.13), which remains valid when the two spheres under consideration have different radii. Similarly to the monodisperse case, it will be convenient to introduce the following auxiliary notation

$$\kappa^p(a) = \kappa^i + \frac{4\kappa^s}{3a}, \tag{58a}$$

$$\tau(a) = \tau^i(a) + \frac{2}{a}\tau^s(a), \tag{58b}$$

$$\tau'(a) = \tau^i(a) - \frac{3}{2}\frac{\kappa^i - \kappa^m}{\kappa^s}\tau^s(a), \tag{58c}$$

so that equation (46) still applies. Substitution of (54), (55), (56), (57) and (58) into (11), finally leads to

$$\frac{1}{2}KE^2 \geq \frac{1}{2}\kappa^m E^2 + \int_0^{+\infty} f(a)\,\tau(a)\,\mathrm{d}a\,E - \frac{1}{2}\int_0^{+\infty} f(a)\frac{\tau(a)^2}{\kappa^p(a) - \kappa^m}\mathrm{d}a - \dots$$
$$\dots - \frac{1}{2}\frac{3}{3\kappa^m + 4\mu^m}\int_0^{+\infty} f(a)\,\tau(a)^2\,\mathrm{d}a + \frac{1}{2}\frac{3}{3\kappa^m + 4\mu^m}\left[\int_0^{+\infty} f(a)\,\tau(a)\,\mathrm{d}a\right]^2, \tag{59}$$

where the optimum choice $\tau' \equiv 0$ has been made. We now seek the scalar polarization $\tau(a)$ which makes the bound on the right-hand side of (59) as large as possible. Stationarity of this bound with respect to τ leads to

$$\int_0^{+\infty} f(a)\,\delta\boldsymbol{\tau}(a)\,\mathrm{d}a\,E - \int_0^{+\infty} f(a)\frac{\tau(a)\,\delta\tau(a)}{\kappa^p(a) - \kappa^m}\mathrm{d}a - \frac{3}{3\kappa^m + 4\mu^m}\int_0^{+\infty} f(a)\,\tau(a)\,\delta\tau(a)\,\mathrm{d}a + \dots$$
$$\dots + \frac{3}{3\kappa^m + 4\mu^m}\int_0^{+\infty} f(a')\,\tau(a')\,\mathrm{d}a'\int_0^{+\infty} f(a)\,\delta\tau(a)\,\mathrm{d}a = 0, \tag{60}$$

where $\delta\tau$ is a small variation of τ. This variation is arbitrary, and (60) therefore reduces to

$$\left[\frac{1}{\kappa^p(a) - \kappa^m} + \frac{3}{3\kappa^m + 4\mu^m}\right]\tau(a) = E + \frac{3}{3\kappa^m + 4\mu^m}\int_0^{+\infty} f(a')\,\tau(a')\,\mathrm{d}a'. \tag{61}$$

The above equation uniquely defines the optimum choice of τ. Indeed, introducing the (as yet unknown) quantity $T = \int_0^{+\infty} f(a)\,\tau(a)\,\mathrm{d}a$, (61) reads

$$\tau(a) = \frac{\kappa^p(a) - \kappa^m}{3\kappa^p(a) + 4\mu^m}\left[(3\kappa^m + 4\mu^m)\,E + 3T\right], \tag{62}$$

which, upon multiplication by $f(a)$ and integration with respect to a results in the following value of T

$$3T = (3\kappa^m + 4\mu^m)\,\frac{F}{1-F}E, \tag{63a}$$

$$F = 3\int_0^{+\infty} \frac{\kappa^p(a) - \kappa^m}{3\kappa^p(a) + 4\mu^m} f(a)\,\mathrm{d}a. \tag{63b}$$

In the above expressions, F, and therefore T depend only upon the material properties κ^i, κ^s, κ^m and μ^m and the particle-size distribution f, which are all *input* data; thus, T is fully determined. Substitution of (63) in (62) and (59) gives the explicit expression of the optimum polarization $\tau(a)$

$$\tau(a) = \frac{\kappa^p(a) - \kappa^m}{3\kappa^p(a) + 4\mu^m}\,(3\kappa^m + 4\mu^m)\,\frac{E}{1-F}, \tag{64}$$

as well as the optimum lower bound on the effective bulk modulus of the composite

$$K \geq \kappa^m + \frac{F}{1-F}\,(3\kappa^m + 4\mu^m). \tag{65}$$

Expression (65) generalizes (50) to polydisperse distributions of inclusions; to the best of our knowledge, this result is new. From the definition of F (63), it is readily seen that the particle size distribution is explicitly accounted for in (65); furthermore, susbtitution of $f(a') \equiv f\delta(a' - a)$ shows as expected that (65) reduces to (50) in the case of monosized inclusions.

Conclusion

In this paper, we introduce the *thin elastic layer analogy* which allows the use of polarization techniques, even when surface stresses occur at the matrix-inclusion boundary. We therefore answer affirmatively the up to now still pending question raised by Le Quang and He [14], on the very possibility of including interface effects into a polarization framework.

We then propose Hashin-Shtrikman type lower bounds on the bulk modulus of a composite made of mono-sized spherical nano-inclusions, taking explicitly interface effects into account. Our results improve on the first-order bounds proposed by Le Quang and He [14], and coincide with the Mori-Tanaka estimate established by Duan et al. [11]. Therefore, this previously known estimate is in fact a rigorous lower-bound on the effective bulk modulus, provided that the stiffness of the interface is positive definite.

This last requirement is not always true [7], in which case inequality (50), or its generalization (65), no longer holds. The quantity on the right hand side can however still be used as an estimate of the effective bulk modulus.

The lower-bound (50) established for monodisperse spherical nano-inclusions can easily be extended to account for polydispersity. We believe that the resulting lower-bound (65) is new; it explicitly features the particle-size distribution, which was to be expected, as interface effects introduce a characteristic length-scale, to which the radius of the inclusions can be compared.

This paper calls for one further remark. In order to establish equation (43), we have assumed the representative volume element to be spherical. It seems therefore that the exact bound depends on the shape of the (albeit large) representative volume element. This is of course highly undesirable, but it can easily be proved that (43) in fact holds for any shape of the domain (see Appendix C).

Appendix A. Equivalence of the interface and the thin elastic layer

It has already been mentioned that direct application of inequality (11) fails with interface effects, because of the 2d nature of the stiffness tensor $\mathbf{c}^s$ of the interface. It is however possible to introduce a fictitious elastic layer of thickness $h \ll a$ and appropriate (3d) elastic constants E and ν. Proving the equivalence of the interface and the resulting thin elastic layer is the purpose of this section.

The 3d equilibrium equations of the thin layer read, in spherical coordinates

$$\partial_r \sigma_{rr} + \frac{1}{r}\,\partial_\theta \sigma_{r\theta} + \frac{1}{r\sin\theta}\,\partial_\varphi \sigma_{r\varphi} + \frac{1}{r}\left(2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\varphi\varphi} + \sigma_{r\theta}\cot\theta\right) = 0, \tag{A.1}$$

$$\partial_r \sigma_{r\theta} + \frac{1}{r}\,\partial_\theta \sigma_{\theta\theta} + \frac{1}{r\sin\theta}\partial_\varphi \sigma_{\theta\varphi} + \frac{1}{r}\left[\left(\sigma_{\theta\theta} - \sigma_{\varphi\varphi}\right)\cot\theta + 3\sigma_{r\theta}\right] = 0, \tag{A.2}$$

$$\partial_r \sigma_{r\varphi} + \frac{1}{r}\,\partial_\theta \sigma_{\theta\varphi} + \frac{1}{r\sin\theta}\,\partial_\varphi \sigma_{\varphi\varphi} + \frac{1}{r}\left(3\sigma_{r\varphi} + 2\sigma_{\theta\varphi}\cot\theta\right) = 0. \tag{A.3}$$

The surface-stress is then defined as the resultant of the stresses within the thickness of the membrane

$$\sigma^s_{ij} = \int_{r=a}^{r=a+h} \sigma_{ij}\,\mathrm{d}r \simeq h\,\sigma_{ij} \qquad (i, j \in \{r, \theta, \varphi\}), \tag{A.4}$$

and integration of equations (A.1), (A.2) and (A.3) with respect to $a \le r \le a+h$ yields, for $h \ll a$

$$[\![\sigma_{rr}]\!] + \frac{1}{a}\,\partial_\theta \sigma^s_{r\theta} + \frac{1}{a\sin\theta}\,\partial_\varphi \sigma^s_{r\varphi} + \frac{1}{a}\left(2\sigma^s_{rr} - \sigma^s_{\theta\theta} - \sigma^s_{\varphi\varphi} + \sigma^s_{r\theta}\cot\theta\right) = 0, \tag{A.5}$$

$$[\![\sigma_{r\theta}]\!] + \frac{1}{a}\,\partial_\theta \sigma^s_{\theta\theta} + \frac{1}{a\sin\theta}\partial_\varphi \sigma^s_{\theta\varphi} + \frac{1}{a}\left[\left(\sigma^s_{\theta\theta} - \sigma^s_{\varphi\varphi}\right)\cot\theta + 3\sigma^s_{r\theta}\right] = 0, \tag{A.6}$$

$$\partial_r \sigma^s_{r\varphi} + \frac{1}{a}\,\partial_\theta \sigma^s_{\theta\varphi} + \frac{1}{a\sin\theta}\,\partial_\varphi \sigma^s_{\varphi\varphi} + \frac{1}{a}\left(3\sigma^s_{r\varphi} + 2\sigma^s_{\theta\varphi}\cot\theta\right) = 0, \tag{A.7}$$

where $[\![\sigma_{ri}]\!]$ here denotes the difference $\sigma_{ri}(r = a + h) - \sigma_{ri}(r = a)$, which reduces to the discontinuity introduced in section 1 when $h \to 0$.

Since σ_{ri} is continuous at $r = a$ and $r = a + h$, we find that σ^s_{ri} scales as $h[\![\sigma_{ri}]\!]$ when $h \to 0$. Equations (A.5) to (A.7) then show that $\sigma^s_{\theta\theta}$, $\sigma^s_{\varphi\varphi}$ and $\sigma^s_{\theta\varphi}$ scale as $a[\![\sigma_{ri}]\!]$. In other words, the normal stresses σ_{ri} can be neglected, and equations (A.5), (A.6) and (A.7) finally reduce to (3), (4) and (5).

Integrating with respect to r the constitutive equations of the membrane, while enforcing $\sigma^s_{rr} = 0$, we get the ‘plane-stress’ equations

$$\sigma^s_{\theta\theta} = \frac{Eh}{1+\nu}\left[\varepsilon_{\theta\theta} + \frac{\nu}{1-\nu}\left(\varepsilon_{\theta\theta} + \varepsilon_{\varphi\varphi}\right)\right], \tag{A.8}$$

$$\sigma^s_{\varphi\varphi} = \frac{Eh}{1+\nu}\left[\varepsilon_{\varphi\varphi} + \frac{\nu}{1-\nu}\left(\varepsilon_{\theta\theta} + \varepsilon_{\varphi\varphi}\right)\right], \tag{A.9}$$

$$\sigma^s_{\theta\varphi} = \frac{Eh}{1+\nu}\,\varepsilon_{\theta\varphi}, \tag{A.10}$$

which are identical to equations (6) through (8), provided that conditions (20) are enforced. The equivalence between the finite thickness elastic membrane and the elastic interface is then established.

Appendix B. Solution to the polarized problem

In this section, we carry out the calculation of $\mathbf{\Gamma}^m_\infty \circledast \boldsymbol{\tau}^p$, where $\boldsymbol{\tau}^p$ is given by (27) and (31). Recalling the definition of $\mathbf{\Gamma}^m_\infty$, as well as Lipmann-Schwinger's equation [18], it is easily found that $-\mathbf{\Gamma}^m_\infty \circledast \boldsymbol{\tau}$ is the strain $\boldsymbol{\varepsilon}(\mathbf{x})$ within the homogeneous, infinite space $\mathbb{R}^3$ (with elastic constants κ^m and μ^m), due to the prestress $\boldsymbol{\tau}^p(\mathbf{x})$

$$\operatorname{div}\left[\mathbf{c}^m : \boldsymbol{\varepsilon}(\mathbf{x}) + \boldsymbol{\tau}^p(\mathbf{x})\right] = 0 \qquad (\mathbf{x} \in \mathbb{R}^3), \tag{B.1}$$

$$\mathbf{u}(\mathbf{x}) \to 0 \qquad (|\mathbf{x}| \to +\infty), \tag{B.2}$$

where $\mathbf{u}(\mathbf{x})$ is the displacement associated with the strain field $\boldsymbol{\varepsilon}(\mathbf{x})$. Given the expression of $\boldsymbol{\tau}^p$, as well as the requirement that $\mathbf{u}$ must *i.* remain finite at the origin, *ii.* tend to zero at infinity, and *iii.* be continuous at the interface $r = a$, we seek $\mathbf{u}$ under the classical form

$$\mathbf{u}^i(\mathbf{x}) = U\,\frac{r}{a}\,\mathbf{n}, \qquad \mathbf{u}^m(\mathbf{x}) = U\,\frac{a^2}{r^2}\,\mathbf{n}, \tag{B.3}$$

with $r = |\mathbf{x}|$, and $\mathbf{n} = \mathbf{x}/r$. Superscript i (inclusion) refers to the region $r < a$, whereas superscript m (matrix) refers to the region $r > a$. It should be noted however that the polarized problem is formulated on a medium with identical elastic constants in both regions. The strains read

$$\boldsymbol{\varepsilon}^i(\mathbf{x}) = \frac{U}{a}\,\mathbf{i}, \qquad \boldsymbol{\varepsilon}^m(\mathbf{x}) = \frac{U}{a}\,\frac{a^3}{r^3}\,(\mathbf{i} - 3\,\mathbf{n} \otimes \mathbf{n}), \tag{B.4}$$

and the constitutive law (taking into account the prestress $\boldsymbol{\tau}^p$) provides the stresses

$$\boldsymbol{\sigma}^i(\mathbf{x}) = \left(3\,\kappa^m\,\frac{U}{a} + \tau^i\right)\mathbf{i}, \tag{B.5a}$$

$$\boldsymbol{\sigma}^m(\mathbf{x}) = 2\,\mu^m\,\frac{U}{a}\,\frac{a^3}{r^3}\,(\mathbf{i} - 3\,\mathbf{n} \otimes \mathbf{n}). \tag{B.5b}$$

In order to enforce the jump conditions (3), (4), (5), the surface stresses must be evaluated. This is straightforward, since the polarized problem is formulated on an homogeneous medium (zero elastic constants of the interface). For this problem, therefore, the elastic part of the surface stresses is zero. The surface stresses reduce to the polarisation $\boldsymbol{\tau}^s$, and equation (3) leads to

$$\frac{U}{a} = -\frac{\tau^i + 2\,\tau^s/a}{3\kappa^m + 4\mu^m}, \tag{B.6}$$

while equations (4) and (5) are identically satisfied; introduction of (B.6) into (B.4) finally gives the expression of $\boldsymbol{\varepsilon} = -\mathbf{\Gamma}^m_\infty \circledast \boldsymbol{\tau}^p$.

We now consider a second sphere, centered at $\mathbf{R}$, and we evaluate the integral

$$\int_{|\mathbf{x}-\mathbf{R}|\leq a} \boldsymbol{\tau}^p(\mathbf{x} - \mathbf{R}) : (\mathbf{\Gamma}^m_\infty \circledast \boldsymbol{\tau}^p)(\mathbf{x})\,\mathrm{d}^3x = -\int_{|\mathbf{x}-\mathbf{R}|\leq a} \boldsymbol{\tau}^p(\mathbf{x} - \mathbf{R}) : \boldsymbol{\varepsilon}(\mathbf{x})\,\mathrm{d}^3x, \tag{B.7}$$

where $\boldsymbol{\varepsilon}$ is given by (B.4) and (B.6). This integral will be evaluated in two specific cases.

If the two spheres coincide. then $\mathbf{R} = 0$, and $\boldsymbol{\varepsilon}(\mathbf{x}) = \boldsymbol{\varepsilon}^i$. We find

$$-\int_{|\mathbf{x}|\leq a} \boldsymbol{\tau}^p(\mathbf{x}) : \boldsymbol{\varepsilon}(\mathbf{x})\,\mathrm{d}^3x = -\int_{|\mathbf{x}|\leq a} \boldsymbol{\tau}^i : \boldsymbol{\varepsilon}^i\,\mathrm{d}^3x - \ldots$$

$$\ldots - \int_{|\mathbf{n}|=1} \boldsymbol{\tau}^s(\mathbf{n}) : \boldsymbol{\varepsilon}^i\,a^2\,\mathrm{d}^2n = 3v\,\frac{\left(\tau^i + 2\,\tau^s/a\right)^2}{3\kappa^m + 4\mu^m}. \quad \text{(B.8)}$$

If the two spheres do not overlap. then $|\mathbf{R}| > 2a$, and $\boldsymbol{\varepsilon}(\mathbf{x}) = \boldsymbol{\varepsilon}^m(\mathbf{x})$. We set $\mathbf{x} = r\,\mathbf{n} + \mathbf{R}$ ($|\mathbf{n}| = 1$). Since $\mathbf{i} : \boldsymbol{\varepsilon}^m(\mathbf{x}) = \operatorname{tr}\boldsymbol{\varepsilon}^m(\mathbf{x}) = 0$ (see (B.5)), (B.7) can be rewritten

$$-\int_{|\mathbf{x}-\mathbf{R}|\leq a} \boldsymbol{\tau}^p(\mathbf{x}-\mathbf{R}) : \boldsymbol{\varepsilon}(\mathbf{x})\,\mathrm{d}^3x = \ldots$$

$$\ldots = -\int_{\substack{r\leq a\\|\mathbf{n}|=1}} \boldsymbol{\tau}^p(r\,\mathbf{n}) : \boldsymbol{\varepsilon}^m(r\,\mathbf{n} + \mathbf{R})\,r^2\mathrm{d}r\,\mathrm{d}^2n = \ldots$$

$$\ldots = a^2\tau^s \int_{|\mathbf{n}|=1} (\mathbf{n}\otimes\mathbf{n}) : \boldsymbol{\varepsilon}^m(a\,\mathbf{n} + \mathbf{R})\mathrm{d}^2n. \quad \text{(B.9)}$$

The subsequent calculations will be performed in spherical coordinates, θ denoting the angle between $\mathbf{R}$ and $\mathbf{n}$. We first find

$$\boldsymbol{\varepsilon}^m(a\,\mathbf{n} + \mathbf{R}) = -\frac{\tau^i + 2\,\tau^s/a}{3\kappa^m + 4\mu^m}\,\frac{a^3}{(R^2 + 2aR\cos\theta + a^2)^{3/2}}\left[\mathbf{i} - 3\,\frac{(\mathbf{R} + a\,\mathbf{n})\otimes(\mathbf{R} + a\,\mathbf{n})}{R^2 + 2aR\cos\theta + a^2}\right], \quad \text{(B.10)}$$

where $R = |\mathbf{R}|$. Total contraction with $\mathbf{n}\otimes\mathbf{n}$ gives

$$(\mathbf{n}\otimes\mathbf{n}) : \boldsymbol{\varepsilon}^m(a\,\mathbf{n} + \mathbf{R}) = -\frac{\tau^i + 2\,\tau^s/a}{3\kappa^m + 4\mu^m}\,\frac{1}{(1 + 2\rho\cos\theta + \rho^2)^{3/2}}\left[1 - 3\,\frac{(1 + \rho\cos\theta)^2}{1 + 2\rho\cos\theta + \rho^2}\right], \quad \text{(B.11)}$$

with $\rho = R/a > 2$. Inserting into (B.9), and integrating with respect to the azimuthal angle, one finds

$$-\int_{|\mathbf{x}|\leq a} \boldsymbol{\tau}^p(\mathbf{x}-\mathbf{R}) : \boldsymbol{\varepsilon}(\mathbf{x})\,\mathrm{d}^3x = -2\pi a^3\,\frac{\tau^s/a\left(\tau^i + 2\tau^s/a\right)}{3\kappa^m + 4\mu^m}\ldots$$

$$\ldots\int_0^\pi \frac{\sin\theta}{(1 + 2\rho\cos\theta + \rho^2)^{3/2}}\left[1 - 3\,\frac{(1 + \rho\cos\theta)^2}{1 + 2\rho\cos\theta + \rho^2}\right]\mathrm{d}\theta. \quad \text{(B.12)}$$

The integral on the right-hand side can be proved to vanish, and it is finally found

$$-\int_{|\mathbf{x}|\leq a} \boldsymbol{\tau}^p(\mathbf{x}-\mathbf{R}) : \boldsymbol{\varepsilon}(\mathbf{x})\,\mathrm{d}^3x = 0. \quad \text{(B.13)}$$

Appendix C. Proof that the bound on K does not depend on the shape of Ω

In this section, we go back to the simplification introduced in (18) in which the representative volume element was assumed to be of ellipsoidal shape. The resulting bound on the macroscopic bulk modulus K of the composite then depends on the Hill tensor $\mathbf{P}^\Omega$ of this ellipsoid, which in turn depends on the aspect ratio of Ω. Therefore, one might be lead to think that the bound proposed in this paper depends on the actual shape of the representative volume element, which would be highly undesirable. Fortunately, this is not true, as will be proved below.

In this section, we discard the asumption that Ω is an ellipsoid. Going back to equation (18), we now replace $\overline{\boldsymbol{\tau}}$ by its value $\overline{\tau}\,\mathbf{i}$, with (see (32))

$$\overline{\tau} = f\left(\tau^i + \frac{2\tau^s}{a}\right). \tag{C.1}$$

This leads to

$$\begin{aligned}\boldsymbol{\Gamma}^0_\infty \circledast \overline{\boldsymbol{\tau}}\,(\mathbf{x}) &= \int_{\mathbf{y}\in\Omega} \boldsymbol{\Gamma}^0_\infty(\mathbf{x}-\mathbf{y}) : \overline{\boldsymbol{\tau}}\,\mathrm{d}^3y \\ &= \overline{\tau} \int_{\mathbf{y}\in\Omega} \boldsymbol{\Gamma}^0_\infty(\mathbf{x}-\mathbf{y}) : \mathbf{i}\,\mathrm{d}^3y,\end{aligned} \tag{C.2}$$

where the integral is to be understood in the sense of the Cauchy principal values. As usual [20], the fourth-rank Green tensor $\boldsymbol{\Gamma}^0_\infty$ is decomposed as follows

$$\boldsymbol{\Gamma}^0_\infty = \mathbf{E}^0\delta\,(\mathbf{x}) + \mathrm{vp}\,\mathbf{F}^0, \tag{C.3}$$

where $\mathbf{E}^0$ is the Hill tensor for spheres, and

$$F^0_{ijkl} = -\left.\partial^2_{jl} g^0_{ik}\right|_{\{ij\},\{kl\}}. \tag{C.4}$$

In (C.4), g^0_{ik} denotes the second-rank Green operator for the infinite medium, and symmetrization with respect to indices (i, j) and (k, l) was performed. It is a matter of simple algebra to show that $\mathbf{F}^0\,(\mathbf{r}) : \mathbf{i}$ is proportional to $\mathbf{i} - 3\mathbf{n} \otimes \mathbf{n}$, where $\mathbf{n} = \mathbf{r}/\,|\mathbf{r}|$. Therefore, the trace of $\mathbf{F}^0\,(\mathbf{r}) : \mathbf{i}$ is null, and

$$\boldsymbol{\tau}\,(\mathbf{x}) : \mathbf{F}^0\,(\mathbf{x}-\mathbf{y}) : \overline{\boldsymbol{\tau}} = 0, \tag{C.5}$$

since $\boldsymbol{\tau}\,(\mathbf{x})$ is proportional to the second-rank identity tensor. In other words,

$$\begin{aligned}\overline{\boldsymbol{\tau} : \left(\boldsymbol{\Gamma}^0_\infty \circledast \overline{\boldsymbol{\tau}}\right)} &= \int_{\mathbf{x}\in\Omega} \boldsymbol{\tau}\,(\mathbf{x}) : \int_{\mathbf{y}\in\Omega} \delta\,(\mathbf{x}-\mathbf{y}) : \mathbf{E}^0 : \overline{\boldsymbol{\tau}}\mathrm{d}^3y\mathrm{d}^3x = \ldots \\ \ldots &= \frac{1}{V}\int_{\mathbf{x}\in\Omega} \boldsymbol{\tau}\,(\mathbf{x}) : \mathbf{E}^0 : \overline{\boldsymbol{\tau}}\mathrm{d}^3x = \overline{\boldsymbol{\tau}} : \mathbf{E}^0 : \overline{\boldsymbol{\tau}}.\end{aligned} \tag{C.6}$$

Recalling that $\mathbf{E}^0$ is the Hill tensor of a sphere, (C.6) shows that (19) holds for any domain Ω; $\mathbf{P}^\Omega$ sould then be replaced by $\mathbf{E}^0$. In equation (43) the representative volume element was assumed to be spherical, which amounted to replacing $\mathbf{P}^\Omega$ with the tensor $\mathbf{E}^0$. The bound (50) is therefore correct, irrespective of the shape of Ω.

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